Thin Film Structures and Low Temperature Electrodes for SOFC's

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Advantages of Thin Film Solid Oxide Fuel Cells

- Reducing the electrolyte thickness in a SOFC decreases the amount of IR losses in the electrolyte
- Reducing the ohmic losses allows the fuel cell to operate at much lower temperatures
- Benefits from reducing the operating temperature include:
  - Metals can be used at the interconnect
  - Less reaction occurs between cell components, increasing cell lifetimes
  - Greater cost effectiveness during operation
- Using nanocrystalline electrolytes can further reduce IR losses
- A reliable, cost effective, industrial scale thin film processing technique is needed to produce thin film electrolytes

Thin Film Polymeric Precursor Spin-Coating Technique*

- Standardized aqueous solutions of cationic salts are mixed in appropriate ratios according to the desired oxide
- Add polymerizable organic
- Condensation polymerization reaction occurs and bonds the cations into the backbone of the polymer
- Polymerization reaction continued over heat until desired viscosity (<100cps) is achieved
- Spin coat polymer precursor on rigid substrate
- Heat substrate with polymer film at 70°C until the film has cured (typically 2 hrs)
- Pyrolize the polymer film at low temperature to yield dense nanocrystalline oxide film
- Repeat depositions until desired oxide film thickness has been reached

**U.S. Patent # 5,494,700*

Polymeric Precursor Spin Coating Technique - YSZ

Zirconium Oxide Dichloride ($ZrOCl_2$) + Distilled H_2O

Gravimetric Standardization

Yttrium Nitrate ($Y(NO_3)_3$) + Distilled H_2O

Gravimetric Standardization

Addition of H_2O, E.G., and Tartaric Acid

Homogeneous Solution

Heat, Stir at ~75°C for 40 hrs

Viscous Precursor

Spin Coat on Rigid Substrate

Cure at 70°C for 2hrs.

Anneal at ~350°C for ~1min

EMARC Facilities & Equipment

Analytical

- X-Ray Diffraction (low and high temperature)
- DTA / TGA (controlled atmosphere)
- Dilatometry (controlled atmosphere)
- Field-emission scanning electron microscopy with EBSP
- Transmission electron microscopy
- Energy dispersive X-Ray microanalysis
- Atomic force microscopy
- Scanning auger spectroscopy / ESCA
- SIMS

Electrical

- 2- and 4-point DC conductivity
- AC impedance spectroscopy
- Thermoelectric power

EMARC Facilities & Equipment

Processing

- High temperature (1900°C) controlled-atm furnaces
- CVD / EVD / PVD with Pt deposition
- Powder processing - Pechini, glycine-nitrate, sol-gel
- Powder Characterization:
  - BET / Surface Area
  - Particle Size Distribution
  - Viscosity / Rheology

Magnetic / Optical

- RAMAN Spectroscopy
- Mössbauer Spectroscopy
- FTIR
- Nuclear Magnetic Resonance

EMARC Facilities & Equipment

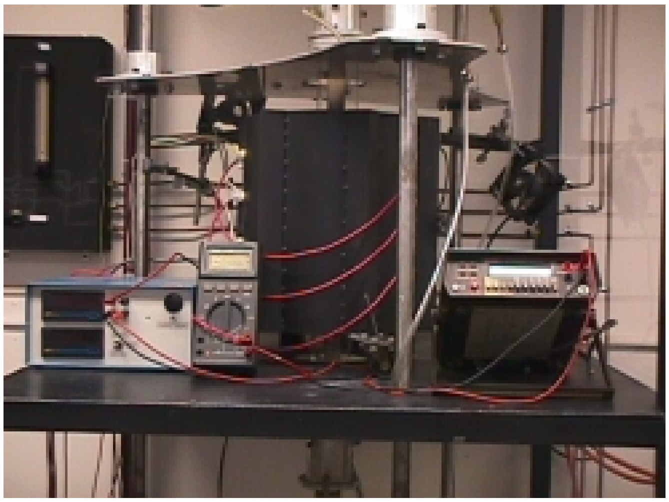
Class 1000 Clean Room

- EMARC has recently invested ≈$200,000 in a class 1000 clean room.
- Equipment in EMARC clean rooms
  - Enclosed Tape Caster
  - Spin Coater
  - Screen Printer
  - Lamination Press

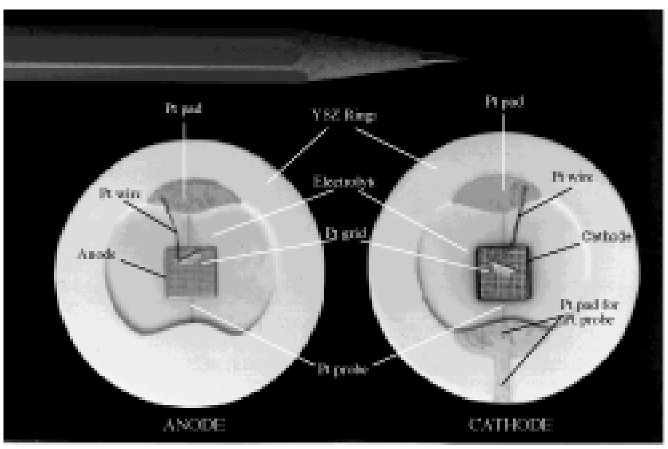
Enclosed glass bed tape caster with hepafilters

Spin Coater

Electrode Testing System

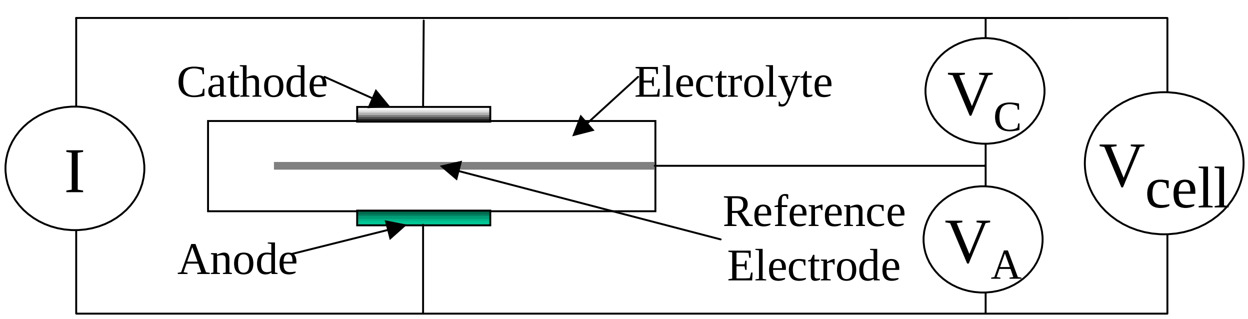


Electrode Testing System



Fuel Cell

- EMARC has the ability to test different electrode materials under fuel cell conditions.
- A reference electrode is buried inside the electrolyte.
- This allows the anode and cathode overpotentials to be separated.



Thin Film SOFC Testing System

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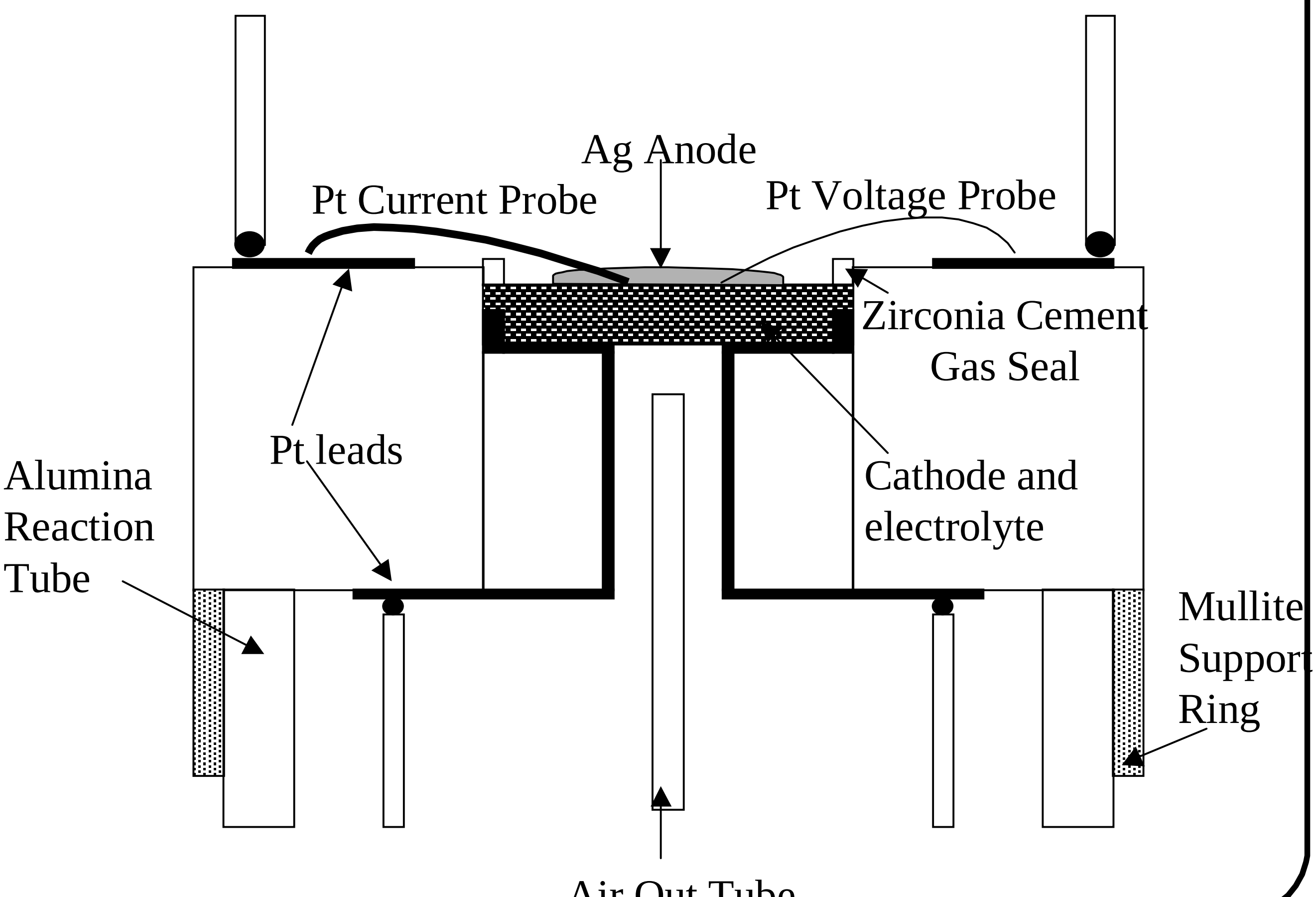
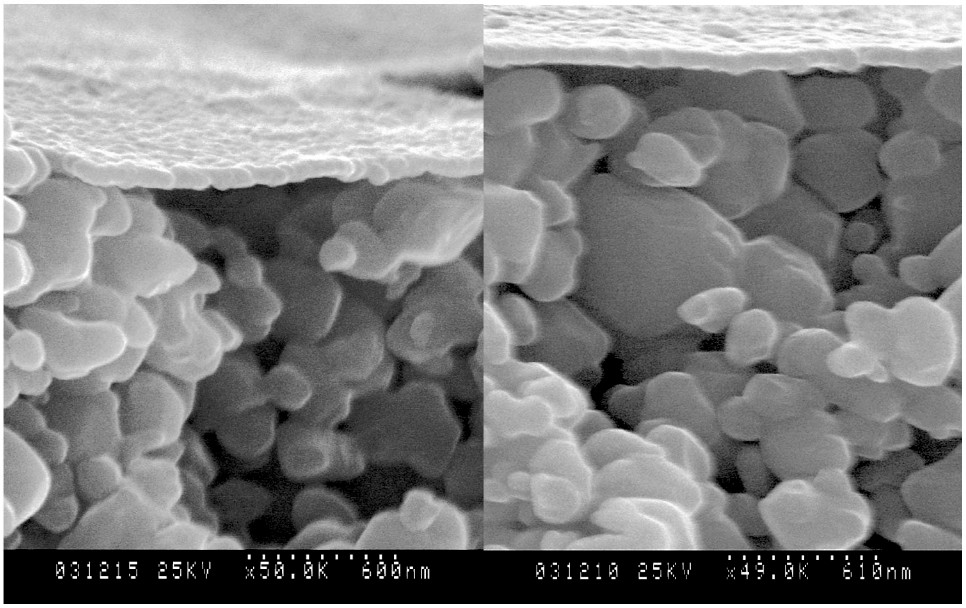


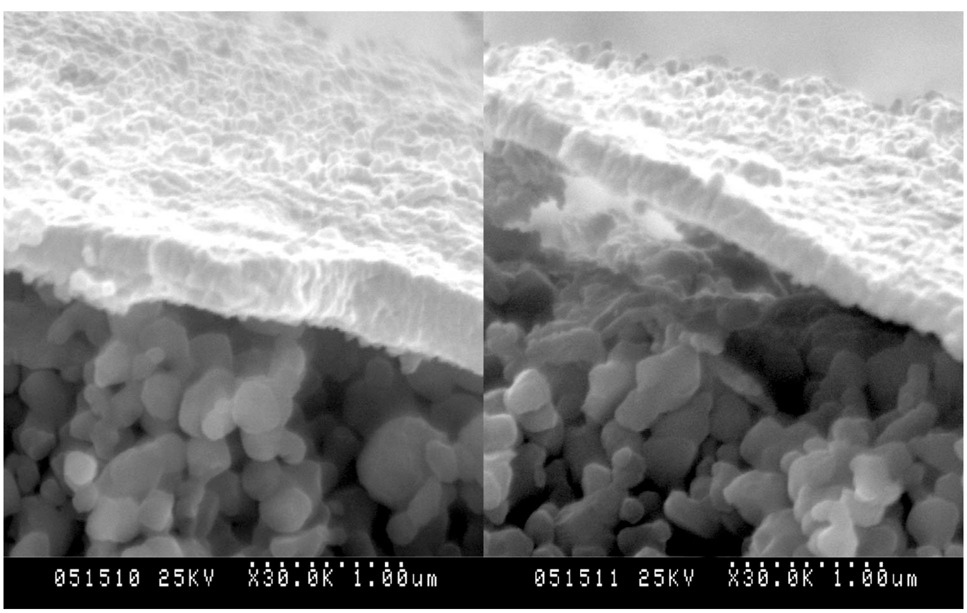
YSZ Thin Film Electrolytes

70nm thick electrolytes on porous NiO/YSZ produced by a thin film transfer technique and annealed at 1000°C



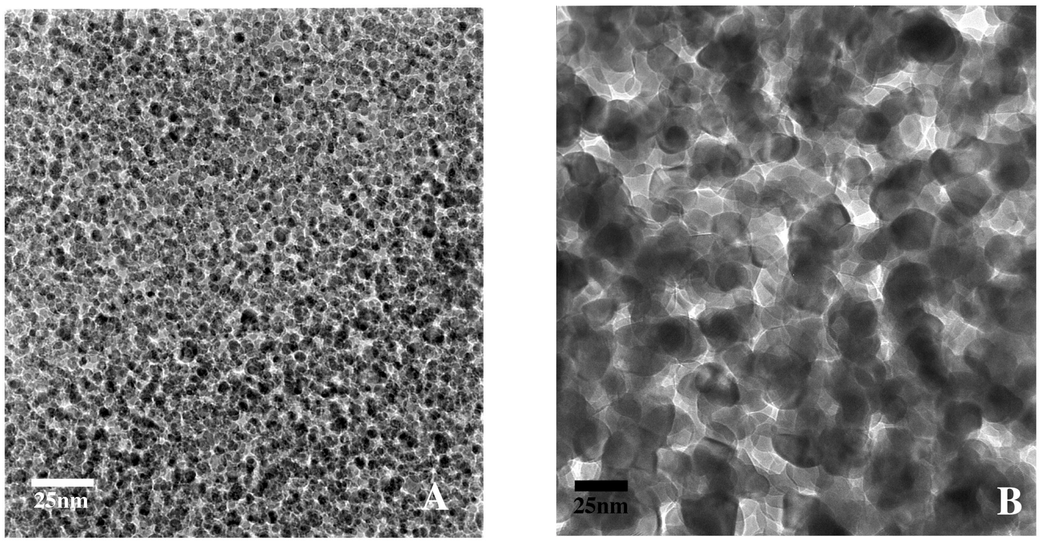
YSZ Thin Film Electrolytes

0.5µm thick electrolytes on porous NiO/YSZ usinga thin film transfer technique and annealed at 1000°C



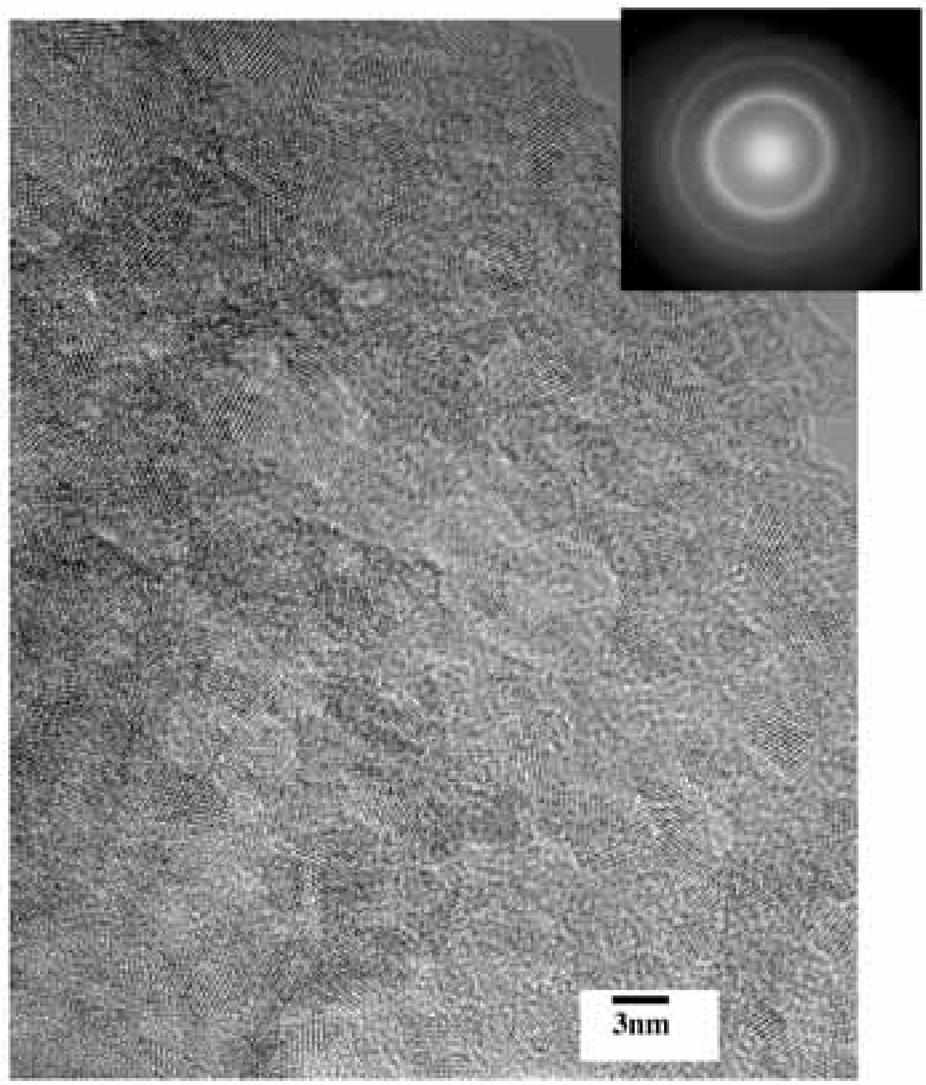
Grain Growth Kinetics

Bright Field TEM micrographs of an unsupported YSZ thin film annealed at A) 600°C and B) 800°C



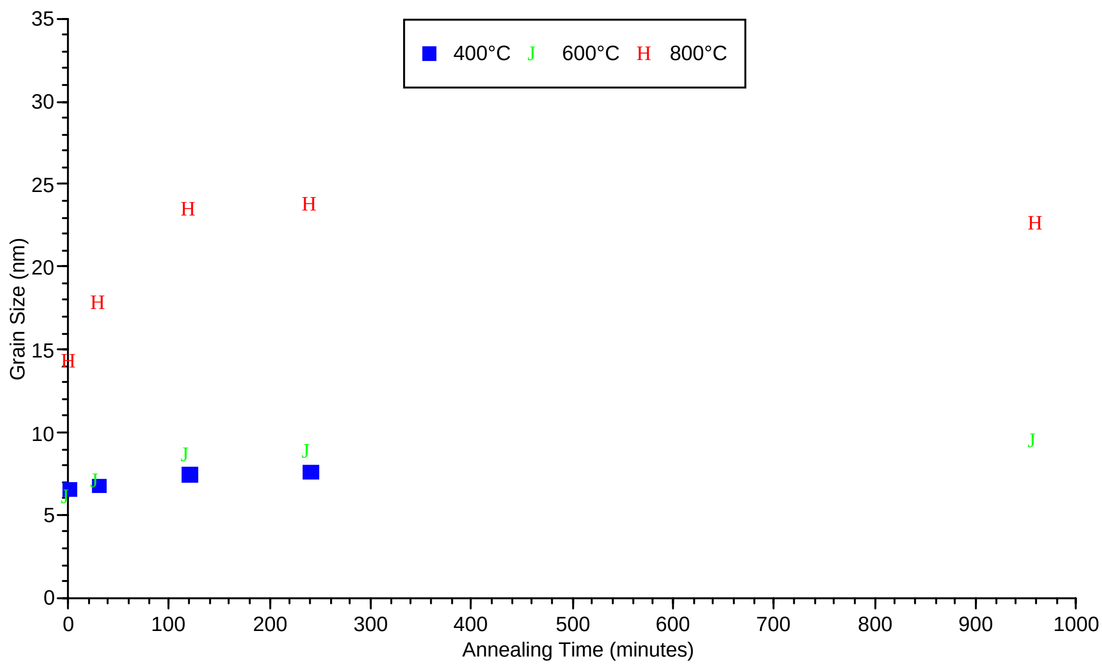
Grain Growth Kinetics

High resolution TEM micrograph and SA diffraction pattern of an unsupported YSZ thin film annealed at 400°C. dg = 5nm

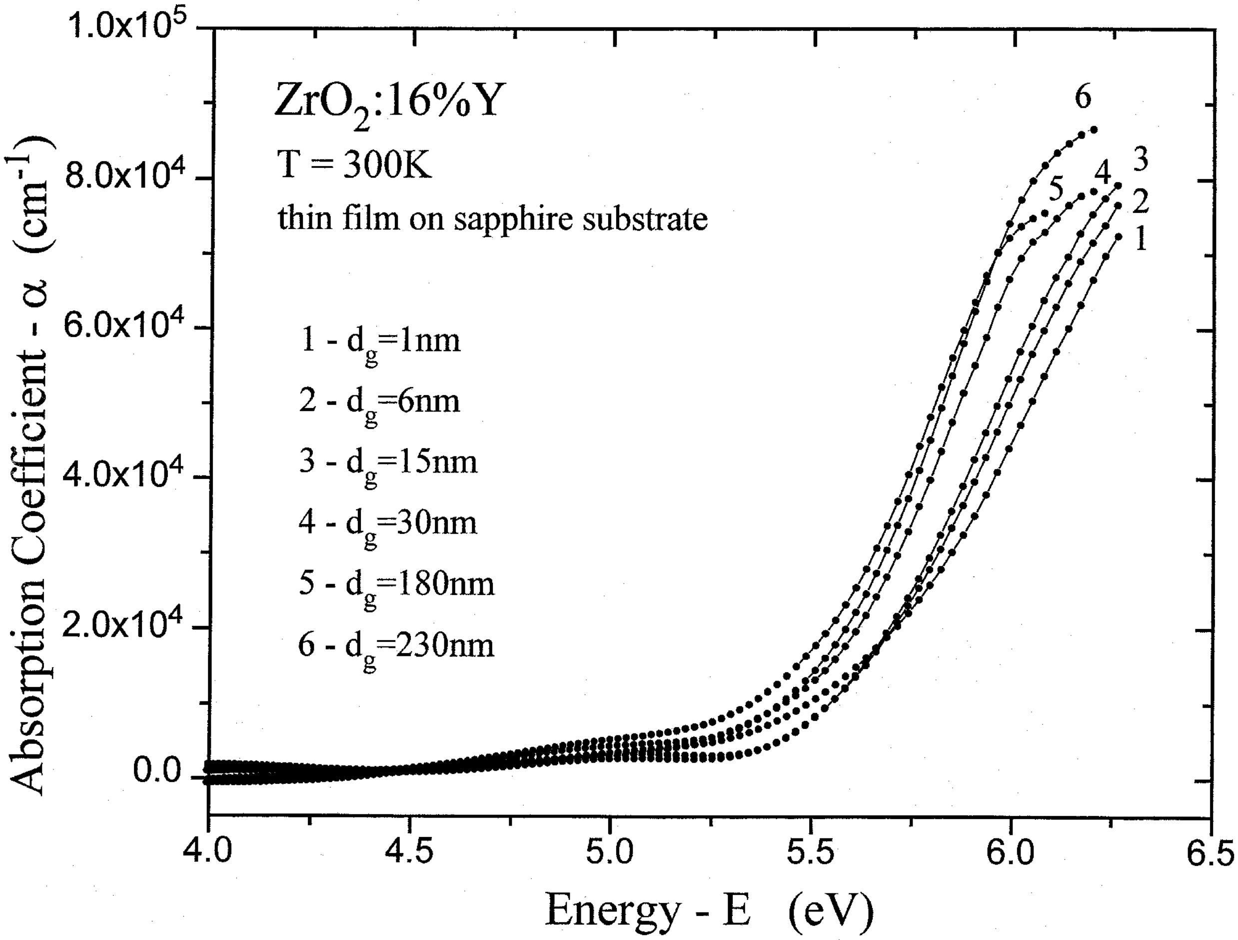


Thin Film Grain Growth

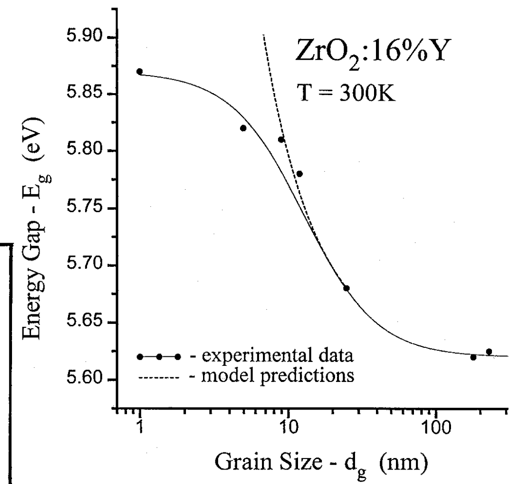
- Unsupported YSZ thin films examined in the TEM after annealing at several temperatures and times
- Grain growth follows a time$^{1/2}$ dependence initially and stabilizes with extended time
- Grain sizes are in the nanocrystalline regime after heat treatments to 800°C

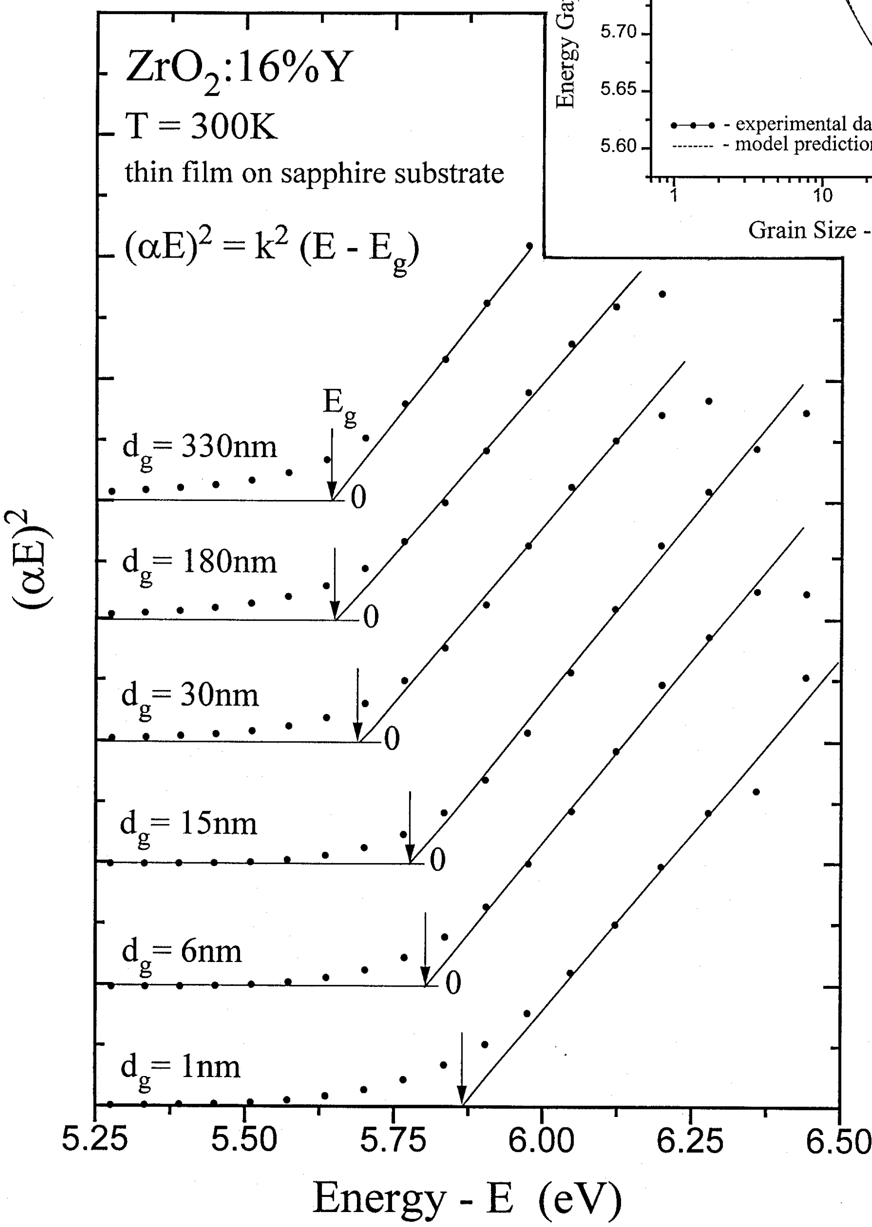


Optical Absorption Measurements on Nanocrystalline YSZ Showed the Band Gap Increased with Decreasing Grain Size• •

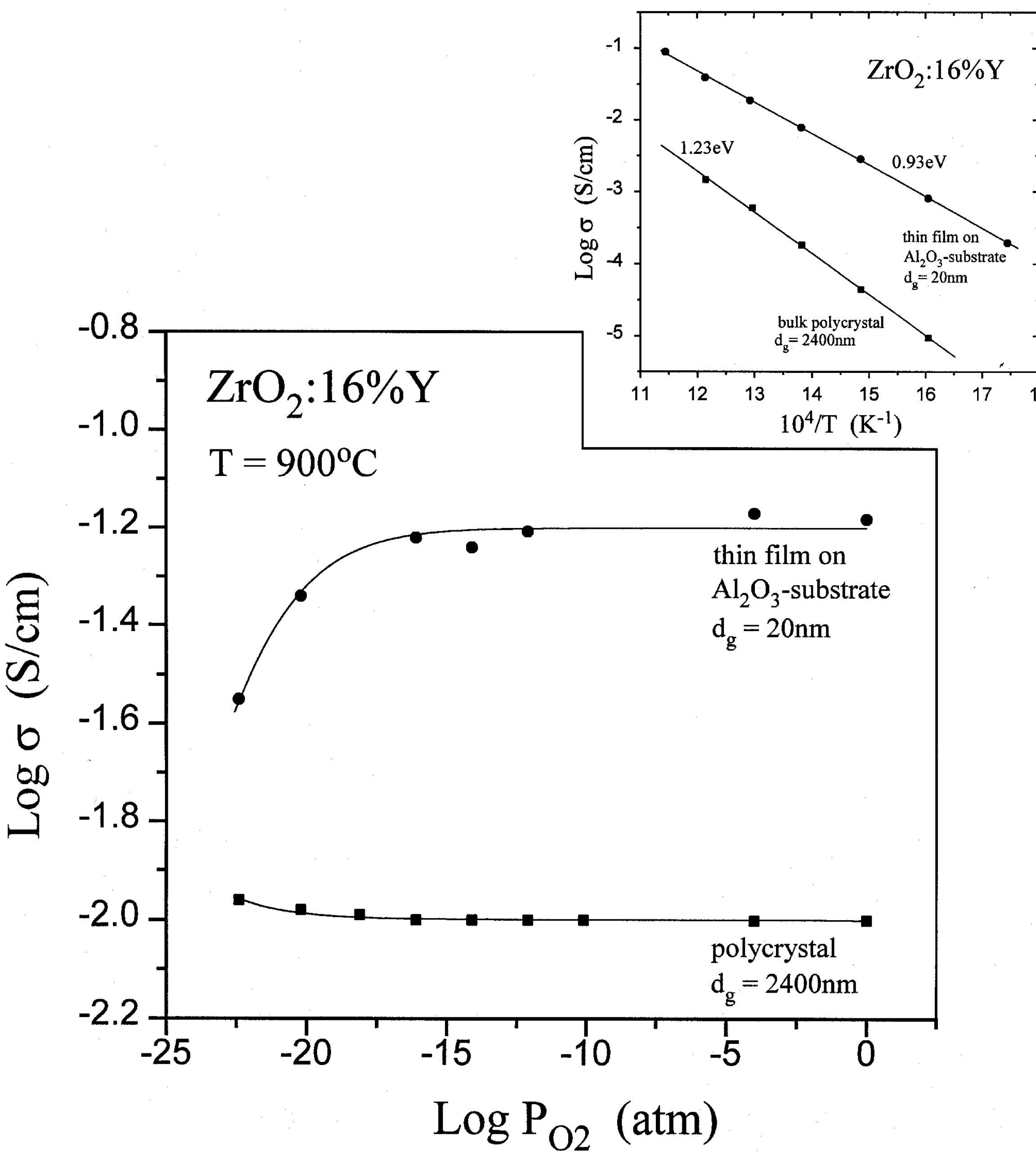


Quantum Confinement in Nanocrystalline YSZ

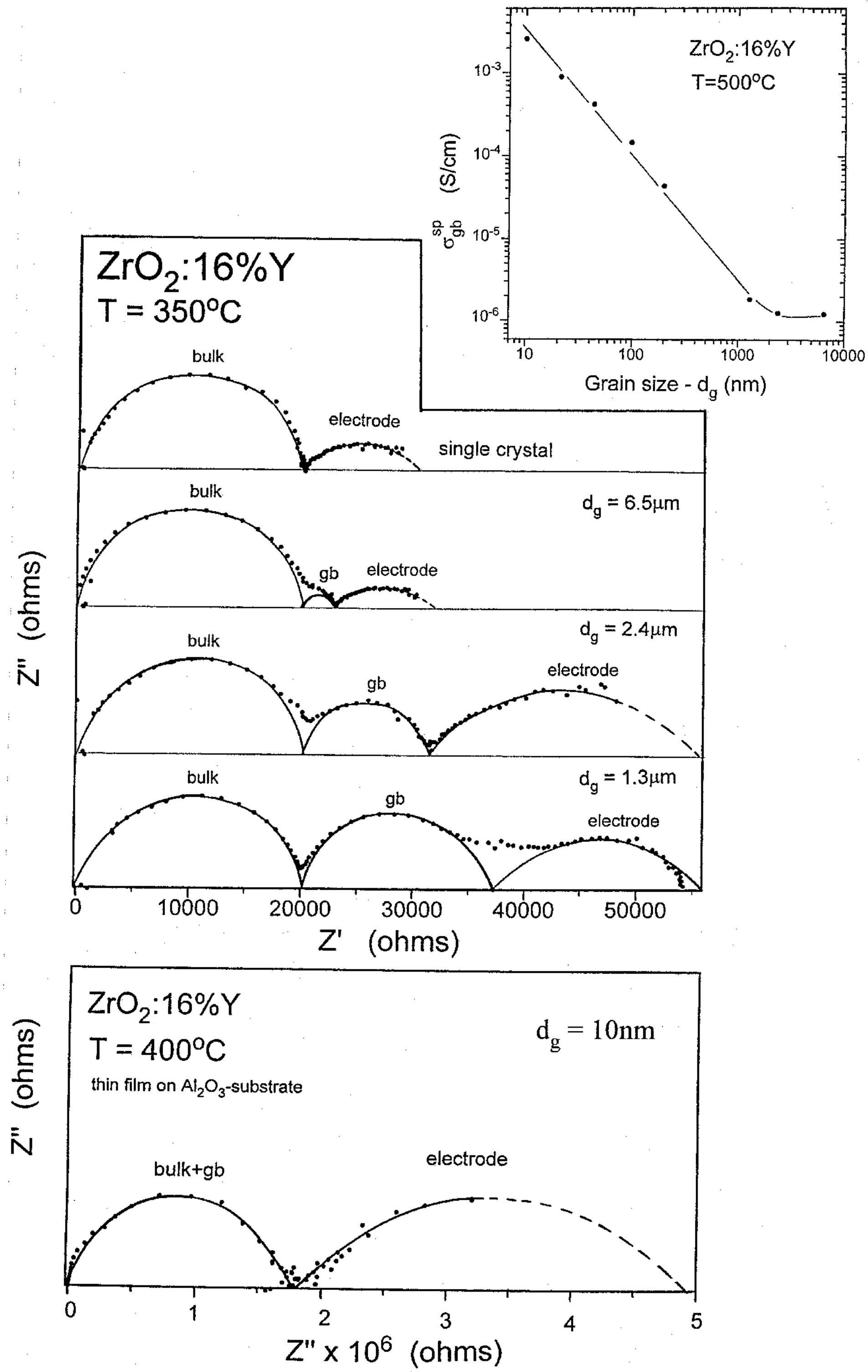




Nanocrystalline YSZ Exhibits an Enhanced Ionic Conductivity: pO_2 dependency



Nanocrystalline YSZ Exhibits an Enhanced Ionic Conductivity: Impedance Spectroscopy



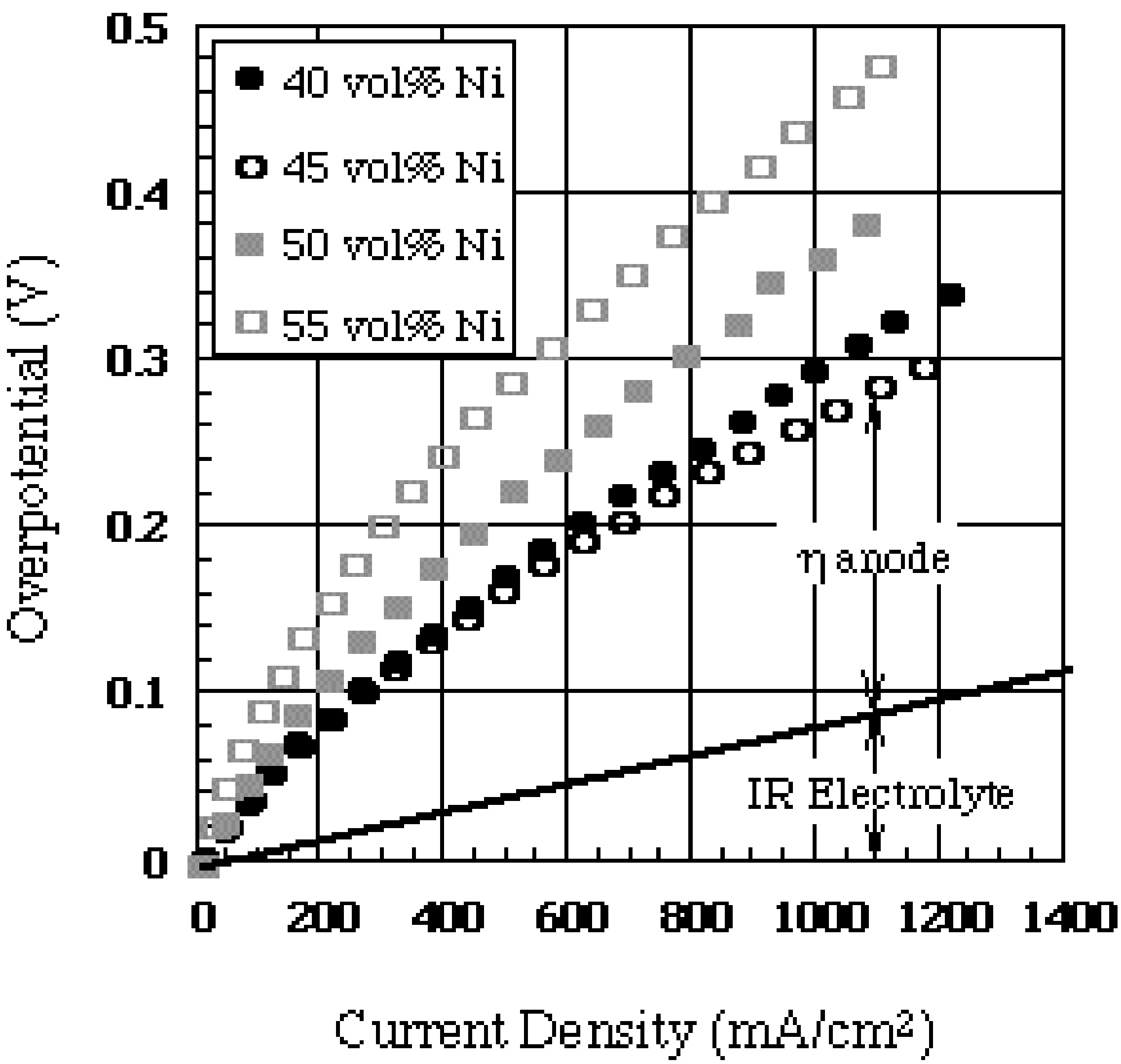
Nanocrystalline YSZ Conductivity Results

- Impedance spectroscopy measurements were performed on YSZ thin films with different annealing temperatures
- As the grain size of nanocrystalline thin films decreases, the electrical conductivity increases
- Due to a higher grain boundary area, the mobility of vacancies increases
- Specific grain boundary conductivity increases due to the segregation of impurities

Nanocrystalline YSZ:

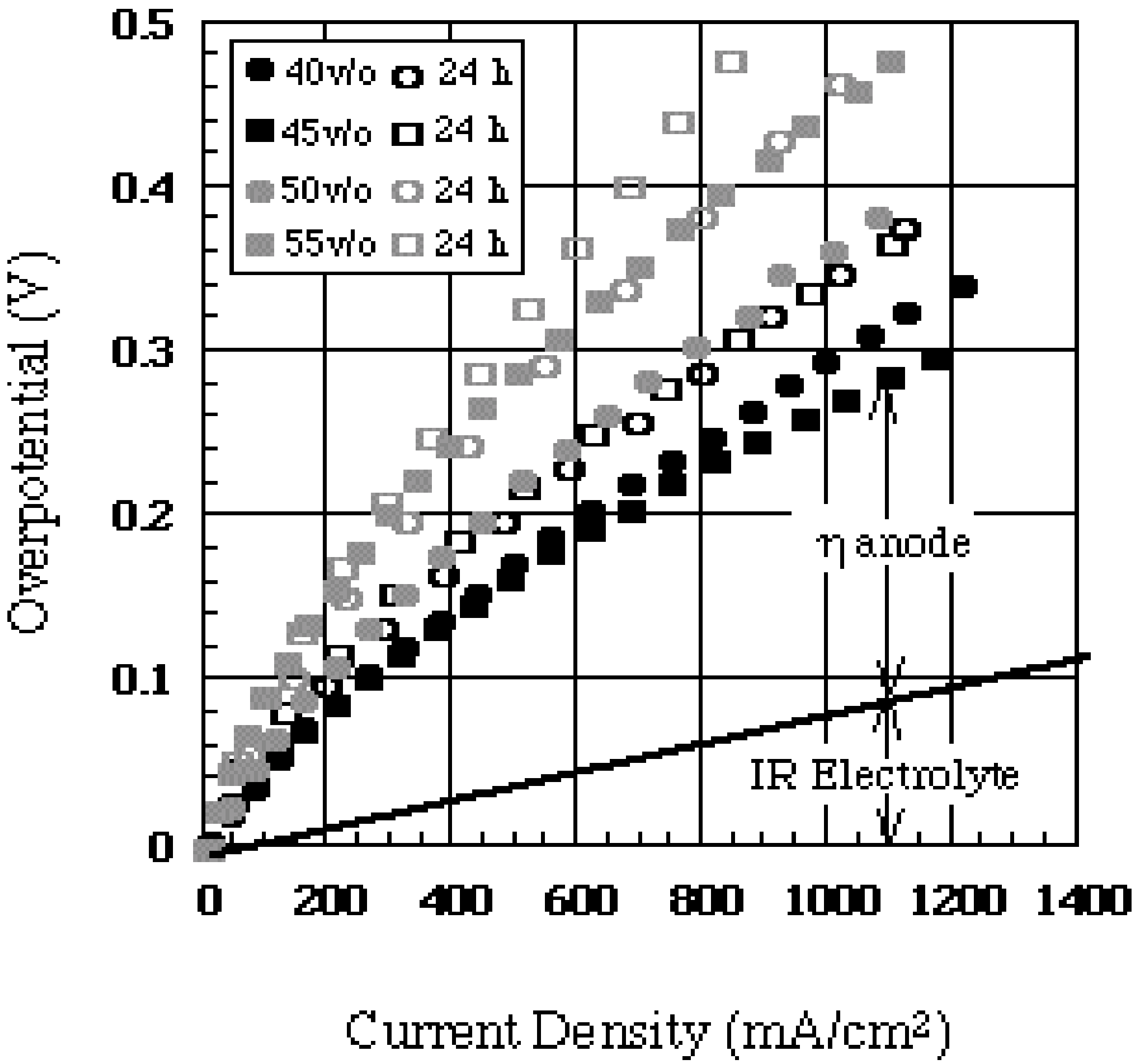
- Optical absorption measurements were used to determine the band gap in YSZ thin films
- As the grain size decreases, the band gap increases, which decreases the electronic conductivity
- Enhanced conductivity in nanocrystalline YSZ thin films is strictly ionic

Influence of Volume % Nickel on the Anodic Overpotential



Initial η-j relations of Ni-YSZ cermets sintered at 1400°C.

Influence of Volume % Nickel on the Anodic Overpotential: Initial and 24h Results



η -j results, initially and after 24 h, for Ni-YSZ cermets sintered at 1400°C.

Summary of Anode Studies

- Compositions studied ranged from 40-55 volume % Ni
- Oxide powder mixtures were calcined at 900ºC, sintered on the electrolyte at 1400ºC, and then reduced in situ.
- The 40 and 45 vol% Ni samples show similar behavior, 220 and 200 mV at 1000mA/cm^2 initially, rising to ≈270 mV/cm^2 after 24 hours.
- The 50 and 55 vol% samples showed much higher overpotentials, both initially and after 24 hours.
- The low vol% Ni samples have lower overpotientials due to the larger YSZ content in the cermet. The increased YSZ reduces the sintering of the nickel particles.

Summary

- EMARC has developed a technique for processing dense, nanocrystalline thin films.
- Research has focused on the electrical and microstructural characterization of solid oxide fuel cell electrolyte and electrode materials.
- Utilizing a transfer technique, fuel cells with thin film electrolytes were produced and tested.

Future Work

- Measure current and voltage performance with different electrolyte thicknesses at low temperatures.
- Develop a measuring protocol for separating overpotientials of the anode and cathode for thin film fuel cells.
- Utilize mixed conductors as electrodes.
- Introduction of interfacial layers to prevent reactions.